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Quiz 29 ANSWERS

1. $E_{n\ell} = -\Re/(n-\delta_\ell)^2$ n is the principal quantum number and δ_ℓ is the quantum defect

A. Explain, based on the effective radial charge distribution of the ion-core, $Z^{eff}(r)$ [$Z^{eff}(r)$ is Z at r = 0 and 1 at r = ∞], why the quantum defect, δ_ℓ, is positive.

As the electron approaches the nucleus, it sees a monotonically increasing Z^{eff}. If Z^{eff} were constant at 1.00, then the quantum defect would be zero. But as Z^{eff} increases above 1, the electron is stabilized relative to the corresponding orbital on Hydrogen. Since $\delta_\ell > 0$ corresponds to stabilization (lowering of $E_{n\ell}$), the monotonically increasing Z^{eff} as $r \to 0$ is consistent with $\delta_\ell > 0$.

B. Predict, based on $Z^{eff}(r)$ and the centrifugal term in the potential $\left[\ell(\ell+1)/2\mu r^2\right]$, whether δ_s is larger or smaller than δ_p. Explain.

The centrifugal barrier keeps the *p* electron at a larger distance from the nucleus, thus the *p* orbital sees a smaller $\langle Z^{eff}(r)\rangle_{np}$ than $\langle Z^{eff}(r)\rangle_{ns}$. This leads to a larger stabilization, hence a larger positive δ_ℓ for *s* than *p*.

C. If $\bar{E}_n = (E_{ns} + E_{np})/2$ and $\Delta = \delta_s - \delta_p$, derive $\Delta E_n \equiv (E_{np} - E_{ns}) \approx \frac{2\Re\Delta}{n^3}$.

$$\Delta E_n = E_{np} - E_{ns} = -\frac{\Re}{(n-\delta_p)^2} + \frac{\Re}{(n-\delta_s)^2} = \frac{\Re}{n^2}\left[\left(1-\frac{\delta_s}{n}\right)^{-2} - \left(1-\frac{\delta_p}{n}\right)^{-2}\right]$$

$$= \frac{\Re}{n^2}\left[\left(1+\frac{2\delta_s}{n}\right) - \left(1+\frac{2\delta_p}{n}\right)\right]$$

$$= \frac{\Re}{n^2}\left[\frac{2\delta_s - 2\delta_p}{n}\right] = \frac{2\Delta\Re}{n^3}$$

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